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The synthesis and characterization of 4-isopropylanilino derivatives of cyclotriphosphazene

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ABSTRACT

Hexachlorocyclotriphosphazene $N_3P_3Cl_6$ and gem-disubstituted cyclotriphosphazene derivatives $N_3P_3Cl_4X_2$ (X = Ph, PhS, PhNH) were reacted with 4-isopropylaniline to give geminal tetra and hexa substituted compounds (**1a–4a**, **1b–4b**). The compounds (**1a–4a**, **1b–4b**) were separated by column chromatography on silica gel and analyzed by elemental analysis, mass spectrometry, and ^{31}P and ^{1}H NMR spectroscopies, and also crystal structures of **2a** and **3b** were determined by X-ray crystallography. Compounds were prepared to cover the normal ranges of C-, S- and N-substituents in cyclophosphazene (X = Cl, Ph, SPh, NHPh). Compounds (**1a–4a**, **1b–4b**) were reported for the first time. We additionally investigated the effect of substituent (Cl, Ph, SPh, NHPh) on ^{31}P NMR chemical shifts of neighboring phosphorus atoms.

1. Introduction

Phosphazenes are cyclic or linear molecules that contain a framework of alternating phosphorus and nitrogen atoms with two substituent groups attached to each phosphorus atom [1]. Cyclic phosphazenes are an important family of inorganic ring systems [2,3] which have attracted the attention of inorganic chemists in recent years because of their applications as flame retardants, antimicrobial agents, lithium-ion batteries, liquid crystals, organic light emitting diodes, membrane hydrogels, drug carriers, surfactants and phase transfer catalysts [4–16]. Also the preparation of new cyclophosphazene derivatives is very straightforward by a substitution reaction of chlorine atoms on the phosphorus and their physical and chemical properties can be tailored via appropriate selection of substituted groups of phosphorus atoms [17–20].

In this work, we report the synthesis of the geminal 4-isopropylanilino substituted derivatives of cyclotriphosphazenes $N_3P_3Cl_4X_2$ (X = Cl, Ph, PhS, PhNH). The structures of obtaining compounds (**1a–4a**, **1b–4b**) were characterized by elemental analysis, mass spectrometry, and ^{31}P and ^{1}H NMR spectroscopies and crystal structures of **2a** and **3b** were also confirmed by X-ray crystallography. In addition, relationships between substituents effect (Cl, Ph, SPh, NHPh) on phosphazene ring and ^{31}P NMR chemical shifts of 4-isopropylanilino substituted phosphorus were obtained for compounds (**1a–4a**) and (**1b–4b**).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd.) was purified by fractional crystallization from hexane. The following chemicals were obtained from Merck; triethylamine (>99%), *n*-hexane (>96%), benzene (⩾99.5%), thiophenol (>98.0%), aniline (>99%), tetrahydrofuran (THF) (⩾99.0%), dichloromethane (⩾99.0%), diethyl ether (⩾99.0%), anhydrous sodium sulfate (⩾99.0%) ethyl acetate (⩾99.0%) and chloroform-d1, from Alfa Aesar; 4-isopropylaniline (>99%) and toluene (>99%). Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh and, Kieselgel 60, 70–230 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length).

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were recorded on a Bruker MicrOTOF LC–MS spectrometer with the electrospray ionization method. ^{31}P and ^{1}H NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer using 85% H_3PO_4 as an external reference for ^{31}P and TMS as an internal reference for ^{1}H.

2.2.1. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer. Absorption correction by multi-scan has been applied [21] and space groups were determined using XPREP implemented

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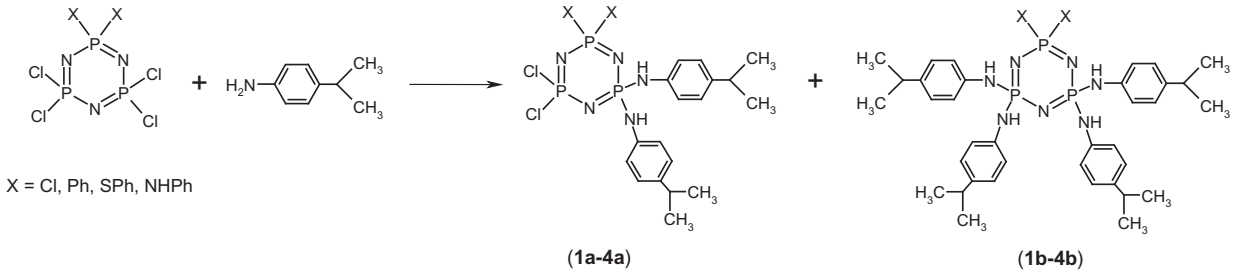

X =	Cl	(**1a**)	Cl	(**1b**)
	Ph	(**2a**)	Ph	(**2b**)
	SPh	(**3a**)	SPh	(**3b**)
	NHPh	(**4a**)	NHPh	(**4b**)

Scheme 1. The synthesis scheme of compounds (**1a**–**4a**, **1b**–**4b**).

in APEX2 [22]. Structures were determined using the direct methods procedure in SHELXS-97 [23] and refined by full-matrix least squares on F^2 using SHELXL-97 [23]. All non-hydrogen atoms were refined with anisotropic displacement parameters and C–H hydrogen atoms were placed in calculated positions and allowed to ride on the parent atoms. The final geometrical calculations and the molecular drawings were carried out with PLATON [24], and MERCURY [25] programs. Structure determinations have been deposited with the Cambridge Crystallographic Data Centre with references CCDC-886526 for structure **2a** and CCDC-886527 for structure **3b**.

2.3. Syntheses

The cyclotriphosphazene derivatives $N_3P_3Cl_4X_2$, (X = Ph, SPh, NHPh), which we used as starting compounds were prepared as given in the literature [26–28]. The reactions of cyclotriphosphazene and gem-disubstituted derivatives of cyclotriphosphazene with 4-isopropylaniline were done and compounds (**1a**–**4a**, **1b**–**4b**) (Scheme 1) were obtained.

2.3.1. Reaction of $N_3P_3Cl_6$ with 4-isopropylaniline to give compounds *1a* and *1b*

Triethylamine (1.60 mL,11.52 mmol) and 4-isopropylaniline (1.58 mL, 11.52 mmol) in 20 mL dry THF were added to a stirred solution of $N_3P_3Cl_6$ (1 g, 2.88 mmol) dissolved in 20 mL dry THF at room temperature under an argon atmosphere. The reaction mixture was refluxed for 8 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (3:1) to give compounds **1a** (0.86 g, 54.9%, mp. 161.3 °C) and **1b** (0.08 g, 3.7%, mp. 212.3 °C).

2.3.2. Reaction of $N_3P_3Cl_4Ph_2$ with 4-isopropylaniline to give compounds *2a* and *2b*

Triethylamine (0.81 mL, 5.80 mmol) and 4-isopropylaniline (0.79 mL, 5.80 mmol) in 10 mL dry toluene were added to a stirred solution of $N_3P_3Cl_4(Ph)_2$ (0.5 g, 1.16 mmol) dissolved in 10 mL dry toluene at room temperature under an argon atmosphere. The reaction mixture was refluxed for 5 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (8:1) to give compounds **2a** (0.23 g, 31.6%, mp. 155.0 °C) and **2b** (0.46 g, 48.1%, mp. 212.3 °C). Compound **2a** was crystallized from hexane-dichloromethane (1:4).

2.3.3. Reaction of $N_3P_3Cl_4(SPh)_2$ with 4-isopropylaniline to give compounds *3a* and *3b*

Triethylamine (0.70 mL, 5.05 mmol) and 4-isopropylaniline (0.68 mL, 5.05 mmol) in 10 mL dry THF were added to a stirred solution of $N_3P_3Cl_4(SPh)_2$ (0.5 g, 1.01 mmol) dissolved in 10 mL dry THF at room temperature under an argon atmosphere. The reaction mixture was refluxed for 10 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:THF (8:1) to give compounds **3a** (0.25 g, 35.8%, oily) and **3b** (0.07 g, 7.8%, mp. 206.5 °C). Compound **3b** was crystallized from hexane–dichloromethane (1:2).

2.3.4. Reaction of $N_3P_3Cl_4(NHPh)_2$ with 4-isopropylaniline to give compounds *4a* and *4b*

Triethylamine (0.76 mL, 5.43 mmol) and 4-isopropylaniline (0.74 mL, 5.43 mmol) in 10 mL dry toluene were added to a stirred solution of $N_3P_3Cl_4(NHPh)_2$ (0.5 g, 1.09 mmol) dissolved in 10 mL dry toluene at room temperature under an argon atmosphere. The reaction mixture was refluxed for 5 days and was followed by TLC, which indicated product and no starting material remaining. Triethylamine hydrochloride was then removed by filtration, and the solvent removed under reduced pressure. The products were isolated by column chromatography using hexane:ethylacetate (3:1) to give compounds **4a** (0.24 g, 15.3%, mp. 209.3 °C) and **4b** (0.36 g, 16.8%, mp. 129 °C).

3. Results and discussion

3.1. Syntheses and characterizations of compounds *1a*–*4a*, *1b*–*4b*

Compounds **1a**–**4a** and **1b**–**4b** were obtained from the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ and gem-disubstituted cyclotriphosphazene derivatives, $N_3P_3Cl_4X_2$ (X = Ph, PhS, PhNH) with 4-isopropylaniline (Scheme 1). In present work, compounds were prepared to cover the normal ranges of Cl-, C-, S- and N-substituents in di- or tetra- substituted 4-isopropylanilino derivatives